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## METHODS AND ELECTROLYTES FOR ELECTRODEPOSITION OF SMOOTH FILMS

### CROSS-REFERENCE TO RELATED APPLICATIONS

This invention claims priority from, and is a continuation in part of, currently pending U.S. patent application Ser. No. 13/367,508, filed Feb. 7, 2012, incorporated herein by reference.

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with Government support under Contract DE-AC0576RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

### BACKGROUND

Electrodeposition is widely used to coat a functional material having a desired property onto a surface that otherwise lacks that property. During electrodeposition, electrically charged reactants in an electrolyte solution diffuse, or are moved by an electric field, to cover the surface of an electrode. For example, the electrical current can reduce reactant cations to yield a deposit on an anode. Or, anions of reactants in the electrolyte solution can diffuse, or be moved by the electric field, to cover the surface of a cathode, where the reactant anions are oxidized to form a deposit on the electrode.

Electrodeposition has been successfully utilized in the fields of abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc. It also occurs in the operation of certain energy storage devices. For example, in the charge process of a metal battery or metal-ion battery, metal ions in the electrolyte move from the cathode and are deposited on the anode. Some organic compounds with unsaturated carbon-carbon double or triple bonds are used as additives in non-aqueous electrolytes and are electrochemically reduced and deposited at the anode surface or oxidized and deposited at the cathode surface to form solid electrolyte interphase layers as protection films on both anode and cathode of lithium batteries. Some other organic compounds with conjugated bonds in the molecules are electrochemically oxidized and deposited at the cathode surface to form electrically conductive polymers as organic cathode materials for energy storage devices.

In most instances, the ideal is a smooth electrodeposited coating. For example, a smoothly plated film can enhance the lifetime of a film used for decoration, wear resistance, corrosion protection, and lubrication. A smoothly plated film is also required for energy storage devices, especially for secondary devices. Rough films and/or dendrites generated on electrode surfaces during the charge/discharge processes of these energy storage devices can lead to the dangerous situations, short-circuits, reduced capacities, and/or shortened lifetimes.

Roughness and/or dendrites can be caused by several reasons, including the uneven distribution of electric current density across the surface of the electrodeposition substrate (e.g., anode) and the uneven reactivity of electrodeposited material and/or substrate to electrolyte solvents, reactants, and salts. These effects can be compounded in the particular case of repeated charging-discharging cycles in energy storage devices. Therefore, a need for improved electrolytes and

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methods for electrodeposition are needed to enhance the smoothness of the resultant film.

### SUMMARY

This document describes methods and electrolytes for electrodeposition that result in self-healing, instead of self-amplification, of initial protuberant tips, which are unavoidable during electrodeposition and which give rise to roughness and/or dendrite formation. For electrodeposition of a first conductive material (C1) on a substrate from one or more reactants in an electrolyte solution, embodiments of the electrolyte solution described herein are characterized by a soluble, surface-smoothing additive comprising cations of a second conductive material (C2), wherein cations of C2 have an effective electrochemical reduction potential (ERP) in the solution lower than that of the reactants.

As used herein, cations, in the context of C1, C2, and/or reactants, refer to atoms or molecules having a net positive electrical charge. In but one example, the total number of electrons in the atom or molecule can be less than the total number of protons, giving the atom or molecule a net positive electrical charge. The cations are not necessarily cations of metals, but can also be non-metallic cations. At least one example of a non-metallic cation is ammonium. Cations are not limited to the +1 oxidation state in any particular instance. In some descriptions herein, a cation can be generally represented as  $X^+$ , which refers generally to any oxidation state, not just +1.

In another example, the reactants might not technically be cations but are positively charged species such as conductive monomers/polymers. During the electrodeposition of a metal cation, the cation gets the electron at the anode and is reduced to metal. When forming a conductive polymer via electrodeposition, it is the conjugated monomer, which can be neutral but with double or triple bonds, that gets the electrons. The conjugated monomer re-arranges the double or triple bonds among the same molecular structure and forms new bonds among different molecules. The formed polymer is either neutral or positively charged when protons are incorporated onto the polymer moiety.

In one embodiment, C1 is a metallic material and the reactants comprise cations of C1. Examples of suitable metallic materials include, but are not limited to, elemental metals or alloys containing Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Bi, Po, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, Pt, Au, and/or Hg. Preferably, C1 is an elemental metal material comprising Li, Zn, Na, Mg, Al, Sn, Ti, Fe, Ni, Cu, Zn, Ag, Pt, or Au.

Alternatively, C1 can comprise an electronic conductive polymer. In such instances, the reactants can comprise monomers of the polymer. The monomers can be conjugated monomers that are reduced at the anode during deposition. Examples of polymers can include, but are not limited to, polyaniline, polypyrrole, polythiophene, poly(3,4-ethylenedioxythiophene). Monomers of these polymers can include, but are not limited to, aniline, pyrrole, thiophene, 3,4-ethylenedioxythiophene, respectively.

In another embodiment, the cations of C2 are metal cations. Examples of metals for cations of C2 include, but are not limited to, Li, Cs, Rb, K, Ba, La, Sr, Ca, Ra, Zr, Te, B, Bi, Ta, Ga, Eu, S, Se, Nb, Na, Mg, Cu, Al, Fe, Zn, Ni, Ti, Sn, Sb, Mn, V, Ta, Cr, Au, Ge, Co, As, Ag, Mo, Si, W, Ru, I, Fc, Br, Re, Bi, Pt, and/or Pd. In preferred embodiments, cations of C2 are cations of Cs, Rb, K, Ba, Sr, Ca, Li.